Electrochemical Characteristics of Polyaniline Modified with Platinum Microparticles for Electrochemical Capacitors

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Abstract

Polyaniline (PANI) films prepared by cyclic voltammetry were modified with Pt microparticles by both potentiostatic and pulse techniques. The electrochemical characteristics of these Pt-modified PANI films were very suitable for the electrochemical capacitors since the insulated property of PANI in the less positive potential region was circumvented by the modification of platinum.

Introduction

Polyaniline (PANI) and their derives were found to exhibit high pseudo-capacitance due to the existence of several oxidation structures in the potential region of water decomposition [1-4]. This material is applicable in the electrochemical (EC) capacitors, especially in the more positive potential range. However, the insulated property of this material in the less positive potential region caused a loss in both double-layer capacitance and faradaic pseudo-capacitance [2]. This phenomenon was modified by doping iridium oxide within the polymer during the electrochemical polymerization [1]. However, there was an irreversible oxidation of PAN due to the presence of oxyiridium species in the high oxidation state (Ir(VI)). In addition, the pseudo-capacitance of this modified PANI in the UPD region is still obviously smaller than that in the more positive potential region. The purpose of this work is to plate platinum within the PANI to increase the pseudo-capacitance of PANI in the UPD region for the application of EC capacitors. The electrochemical and textural characteristics of these Pt-modified PANI were also systematically investigated in this work.

Results and Discussion

Polyaniline was modified with platinum micro-particles by the electroplating via either potentiostatic or normal pulse techniques. Typical cyclic voltammogram of a PANI film polymerized from a 1 M HCl solution containing 0.1 M aniline by cyclic voltammetry (60 cycles) is shown as curve 1 in Fig. 1. In addition, the CV curve of this polymer modified by the potentiostatic plating from a 0.1 M HCl solution with 15 g dm^{-3} H_2PtCl_6 at –270 mV (vs. Ag/AgCl) for 10 C cm^{-2} is also shown as curve 2. Moreover, curves 3 and 4 are the CV curves of this polymer modified with Pt by the normal pulse deposition with 1- and 2-second periods of electroplating, respectively. The total charge of both films is the same (10 C cm^{-2}). Four processes of the PANI redox transition are clearly found on curve 1. (*i*) the passive responses in the potential ranges respectively from –200 to 100mV and from –100 to –200mV on the positive and negative sweeps are due to the fact that leucoemeraldine form is in an insulated state. (*ii*) Two redox peaks are clearly found at ca. 50 and 250mV on the negative and positive sweeps, respectively. These peaks are attributed to the redox conversion of PANI from an insulated state (leucoemeraldine form) to a conducting state (polaronic emeraldine form) [9, 16, 21, 22]. (*iii*) Very large background currents, not attributable to the double-layer charging and discharging processes, are found in the potential range from 400 to 650mV and from 650 to 300mV on the positive and negative sweeps, respectively. (*iv*) Anodic currents rise gradually with the positive shift in electrode potentials at potentials positive to 650mV on the positive sweep while the corresponding reduction peak is found in the same potential region on the negative sweep. This pair of redox peaks is attributed to the redox transition between the polaronic emeraldine form and the bipolaronic pernigraniline form. From a comparison of curves 1-4, the UPD hydrogen responses are obviously found between –200 and 100 mV. Accordingly, PANI-modified Pt films exhibit considerable pseudo-capacitance in this potential region, which is very different from the voltammetric responses on curve 1. Therefore, these PANI-modified Pt materials are believed to be more suitable for the application of EC capacitors.

References

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Acknowledgments—The financial support of this work, by the National Science Council of the Republic of China, is gratefully acknowledged.

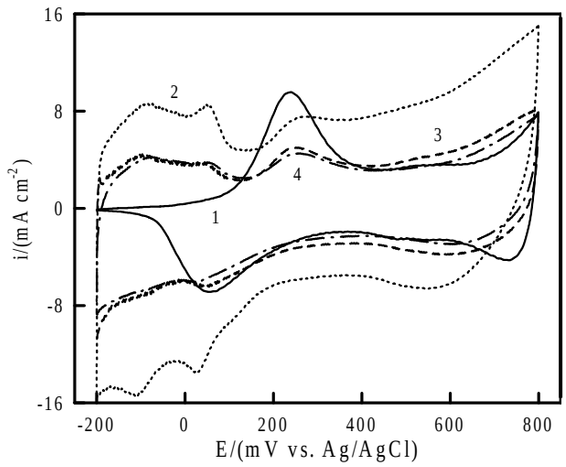

Fig. 1 Cyclic voltammograms of (1) PANI, modified with Pt micro-particles electroplated from a 0.1M HCl solution with 15 g dm^{-3} H_2PtCl_6 by potentiostatic deposition at (2) –270 mV and normal pulse deposition at –270 mV for (3) 1-second plating; and (4) 2-second plating.